

SPECIFICATION

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A CATALYST SYSTEM FOR THE REDUCTION OF NO_x AND NH₃ EMISSIONS

Background of Invention

[0001] 1. Field of the Invention

[0002] The present invention is directed to a catalyst system to facilitate the reduction of nitrogen oxides (NO_x) and ammonia from an exhaust gas. More particularly, the catalyst system of this invention includes a lean NO_x trap in combination with an ammonia selective catalytic reduction (NH₃-SCR) catalyst, which stores the ammonia formed in the lean NO_x trap during rich air/fuel operation and then reacts the stored ammonia with nitrogen oxides to improve NO_x conversion to nitrogen when the engine is operated under lean air/fuel ratios. In an alternate embodiment, a three-way catalyst is designed to produce desirable NH₃ emissions at stoichiometric conditions and thus reduce NO_x and NH₃ emissions.

[0003] 2. Background Art

[0004] Catalysts have long been used in the exhaust systems of automotive vehicles to convert carbon monoxide, hydrocarbons, and nitrogen oxides (NO_x) produced during engine operation into non-polluting gases such as carbon dioxide, water and nitrogen. As a result of increasingly stringent fuel economy and emissions standards for car and truck applications, it is preferable to operate an engine under lean conditions to improve vehicle fuel efficiency and lower CO₂ emissions. Lean conditions have air/fuel ratios greater than the stoichiometric ratio (an air/fuel ratio of 14.6), typically air/fuel ratios greater than 15. While lean operation improves fuel economy, operating under lean conditions increases the difficulty in treating some

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[0006] Lean NOx traps, however, often have the problem of low NOx conversion; that is, a high percentage of the NOx slips through the trap as NOx. NOx slip can occur either during the lean portion of the cycle or during the rich portion. The lean NOx slip is often called "NOx breakthrough". It occurs during extended lean operation and is related to saturation of the NOx trap capacity. The rich NOx slip is often called a "NOx spike". It occurs during the short period in which the NOx trap transitions from lean to rich and is related to the release of stored NOx without reduction. Test results depicted in Figure 1a have shown that during this lean-rich transition, NOx spikes, the large peaks of unreacted NOx, accounts for approximately 73% of the total NOx emitted during the operation of a lean NOx trap. NOx breakthrough accounts for the remaining 27% of the NOx emitted.

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not been a viable solution to achieve 90+% net NOx conversion.

[0010] Accordingly, a need exists for a catalyst system that eliminates NOx breakthrough during the lean operation as well as the NOx spikes during the lean-rich transition period. There is also a need for a catalyst system that is capable of improving net NOx conversion. Finally, there is a need for a catalyst system capable of reducing ammonia emissions.

Summary of Invention

[0011] This invention provides a solution for all of the above problems and, in particular, reduces or eliminates ammonia emissions and improves the net NOx conversion of the catalyst system. These problems are solved by simultaneously removing ammonia and enhancing NOx conversion with the use of an NH_3 -SCR catalyst placed downstream of the lean NOx adsorber catalyst, as shown in Figure 2. The NH_3 -SCR catalyst system serves to adsorb the ammonia emissions from the upstream lean NOx adsorber catalyst generated during the rich pulses. Accordingly, as shown in Figure 2, the ammonia emissions produced by the lean NOx adsorber is stored and effectively controlled by the NH_3 -SCR catalyst rather than being emitted. This reservoir of adsorbed ammonia then reacts directly with the NOx emitted from the upstream lean NOx adsorber. As a result, as shown in Figure 3, the overall net NOx conversion is enhanced from 55% to 80%, while depleting the stored ammonia, as a function of the SCR reaction: $\text{NH}_3 + \text{NOx} \rightarrow \text{N}_2$. The NH_3 -SCR catalyst is then replenished with ammonia by subsequent rich pulses over the lean NOx adsorber.

[0012] During the lean cycle for this lean NOx adsorber + NH_3 -SCR system, the NOx breakthrough from the upstream lean NOx adsorber is reduced continuously as it passes over the NH_3 -SCR until the reservoir of ammonia is depleted. In addition, during the rich cycle, large spikes of unreacted NOx are created. The downstream NH_3 -SCR catalyst thus serves to dampen these large NOx spikes by reacting the unreacted NOx with the reservoir of stored ammonia emitted from the lean NOx adsorber. In general, the combination of the lean NOx adsorber + NH_3 -SCR catalyst system allows for the reduction, or elimination, of ammonia emissions and NOx slip, i.e., reduction of NOx breakthrough and NOx spikes and, therefore, improved net NOx conversion during lean and rich operation.

[0013] Additionally, under this invention, urea and/or ammonia does not need to be injected into the exhaust system to effectuate the reaction between NOx and ammonia. Rather, the ammonia is automatically generated from the NOx present in the exhaust gas as it passes over the precious metal lean NOx adsorber during the rich pulses. The generated ammonia is then stored on the downstream NH_3 -SCR catalyst, to react with the unreacted NOx, and thereby convert the unreacted NOx to nitrogen.

[0014] The NH_3 -SCR catalyst thus serves to adsorb the ammonia from the upstream lean NOx adsorber catalyst generated during the rich pulses. Under this system, the ammonia is stored and effectively controlled rather than being emitted. This reservoir of adsorbed ammonia then reacts directly with any NOx emitted from the upstream lean NOx adsorber. As a result, the overall net NOx conversion is enhanced from 55% to 80%, while the overall gross NOx conversion is enhanced from 68% to 82%, as shown in Figure 3.

[0015] In one alternative embodiment of this invention, the catalyst system can be optimized and NOx reduction increased by vertically slicing the lean NOx trap and NH_3 -SCR catalyst substrates to create separate catalyst zones, such that the catalytic converter shell or can would have alternating sections of lean NOx trap and NH_3 -SCR catalysts, as shown in Figure 4. Under this embodiment, both technologies, the lean NOx trap formulation and the NH_3 -SCR formulation, can be incorporated into a single substrate and/or a single converter can rather than placing the NH_3 -SCR catalyst downstream of the lean NOx adsorber as two separate and distinct catalyst substrates.

Brief Description of Drawings

[0016] Figure 1a is a graph illustrating the NOx spikes that occur during the NOx trap lean-rich transition;

[0017] Figure 1b is a graph illustrating NOx and NH_3 emissions from a typical prior art lean NOx adsorber system;

[0018] Figure 2 depicts the lean NOx and NH_3 -SCR catalyst system of the present invention;

- [0019] Figure 3 depicts reduced NOx emissions and NH₃ emissions as a result of the use of the lean NOx and NH₃-SCR catalyst system of the present invention, as shown in Figure 2;
- [0020] Figure 4 depicts three different zoned catalyst embodiments of the lean NOx and NH₃-SCR catalyst system;
- [0021] Figure 5 is a graph illustrating the reduced levels of NOx and NH₃ emissions resulting from each of the three zoned catalyst embodiments depicted in Figure 4 at a 250 ° C inlet gas temperature and operating at a 50 second lean cycle and 5 second rich cycle;
- [0022] Figure 6 is a graph illustrating the reduced levels of NOx and NH₃ emissions resulting from each of the three zoned catalyst embodiments depicted in Figure 4 at a 200 ° C inlet gas temperature and operating at a 25 second lean cycle and a 5 second rich cycle;
- [0023] Figure 7 shows three proposed examples of washcoat configurations incorporating the lean NOx trap and NH₃-SCR formulations into the same substrate;
- [0024] Figure 8 is a graph illustrating the impact of NOx conversion after hydrothermal aging; and
- [0025] Figure 9 depicts a modified three-way catalyst and NH₃-SCR catalyst system of the present invention.

Detailed Description

- [0026] In this invention, net NOx conversion is improved and ammonia emissions reduced through the use of a lean NOx trap and NH₃-SCR catalyst system which operate together to produce and store ammonia and reduce NOx to nitrogen. In so doing, the catalyst system of the present invention solves three problems of lean NOx traps; namely, reducing NOx breakthrough, NOx spikes and ammonia emissions.
- [0027] In order to meet increasingly stringent fuel economy standards, it is preferable to operate an automotive engine under lean conditions. However, while there is improvement in fuel economy, operating under lean conditions has increased the

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[0028] Throughout this specification, NO_x refers to nitrogen oxides, which include nitrogen monoxide NO and nitrogen dioxide NO₂. Further, lean NO_x adsorber and lean NO_x trap are used interchangeably throughout this specification.

[0029] To achieve NOx reduction, under lean operating conditions, one option is the inclusion of a lean NOx trap. While the lean NOx trap is generally effective in NOx reduction, lean NOx traps are known to have the problems referred to as "NOx slip" which includes breakthrough of NOx during the extended lean operation of the NOx trap and also NOx spikes generated during the transition from the lean to the rich cycle.

[0030] NOx spikes, or NOx emissions during the lean-rich transition, are believed to occur due to the exothermic heat generated from the oxidation of reductants, carbon monoxide, hydrocarbons and hydrogen, by the oxygen released from the oxygen storage material – the temperature rise can be as high as 80–100 °C.

[0031] The problem of NO_x spikes is illustrated in Figure 1a, and the problem of insufficient net NO_x conversion is illustrated in Figure 1b. Figure 1b depicts laboratory reactor data of a lean NO_x adsorber system operating in an 85 second lean and 5 second rich cyclic pattern. The plot in Figure 1b shows the nitrogen species concentration as a function of time. The laboratory reactor data depicted in Figure 1b resulted from a catalyst having an engine swept volume (ESV) of 100%. Additionally, the reactor used to obtain the results in Figure 1b was at a temperature of 300 °C. To begin the cycle, 500 ppm of nitrogen oxide was fed into the reactor where much of it was stored during the 85 second lean duration. During the 5 second rich duration, nitrogen oxide was reduced; however, a significant amount of ammonia was formed. As illustrated in Figure 1b, the data shows ammonia spikes as high as 600 ppm under typical lean NO_x adsorber operation. Conversion, however, is generally improved as the λ ratio is decreased during the rich pulse. Decreasing the λ ratio also leads to

significant production of ammonia and thus results in high gross NOx conversion ($\text{NOx} \rightarrow \text{N}_2 + \text{NH}_3$), but much lower net NOx conversion ($\text{NOx} \rightarrow \text{N}_2$). As illustrated in Figure 1b, the net NOx conversion to nitrogen for this lean NOx adsorber system was only 55%.

[0032] Under the catalyst system of this invention, ammonia is reduced and the net NOx conversion improved simultaneously by placing an NH_3 -SCR catalyst formulation downstream of the lean NOx adsorber catalyst, as shown in Figure 2.

[0033] Figure 2 is an illustration of the catalyst system of this invention, which is capable of simultaneously eliminating ammonia emissions and improving net NOx conversion. As illustrated in Figure 2, NOx produced during engine operation is stored by the lean NOx adsorber during the lean cycle. Following the lean cycle, during the rich cycle of the lean NOx adsorber, NOx is reduced and ammonia generated. The lean NOx adsorber stores much of the NOx during the lean operation and then reduces NOx during rich pulses of the reductants. During the same rich pulses, significant amounts of ammonia are generated, as further illustrated in Figure 1. As illustrated in Figure 2, the lean NOx adsorber emits NO, NO_2 , NH_3 , and N_2O . These same gases then pass through the NH_3 -SCR, where NH_3 is stored. Accordingly, the addition of the NH_3 -SCR catalyst downstream allows for the adsorption of NH_3 and subsequent reaction with any NOx that slips through the upstream lean NOx adsorber, which thus improves the overall net NOx conversion ($\text{NH}_3 + \text{NO} \rightarrow \text{N}_2$). As can be seen in Figure 2, the catalyst system of this invention results in a significant net NOx conversion improvement, the elimination of ammonia emissions, and the production of non-polluting gases nitrogen and N_2O .

[0034] It should be noted that for diesel applications, lean NOx adsorbers must operate at lower temperatures compared to gasoline lean NOx adsorbers since the exhaust temperatures of diesel engines are significantly lower. More ammonia is generated at 200 °C than at 300 °C over lean NOx adsorbers, and thus the catalyst system of this invention has an even greater potential for diesel applications. Likewise, the problem of NOx spikes is more critical at higher temperatures, the temperatures used for gasoline applications; and thus the catalyst system of this invention is beneficial to control the unreacted NOx spikes that result from the operation of a lean NOx

adsorber at operating temperatures typical for gasoline lean NOx adsorber applications.

[0035] The NH_3 -SCR catalyst thus serves to adsorb the ammonia produced naturally from the upstream lean NOx adsorber catalyst generated during the rich pulses. As a result, the NH_3 -SCR catalyst stores the ammonia, controlling it rather than allowing it to be emitted into the atmosphere. This reservoir of adsorbed NH_3 in the NH_3 -SCR catalyst reacts directly with the NOx emitted from the upstream lean NOx adsorber (trap).

[0036] In general, this invention works to clean NOx emissions – and thus has applicability for stationary sources as well as for moving vehicles. This invention may be used to reduce NOx emissions for nitric acid plants, or any other stationary source that requires the reduction of NOx emissions. This invention is nonetheless particularly directed for use with gasoline and diesel vehicles which, unlike stationary sources, have a wide range of operating parameters, especially temperature parameters – which cannot be precisely controlled. The present invention has the ability to store large quantities of ammonia across a broad temperature range to effectuate the reaction between ammonia and nitrogen oxides and thereby convert NOx to nitrogen.

[0037] As illustrated in Figure 3, laboratory experiments have demonstrated that the use of a lean NOx adsorber plus NH_3 -SCR catalyst system improves net NOx conversion from 55%, as illustrated in Figure 1, to 80%. Figure 3 is a graph displaying laboratory data obtained using the catalyst system of this invention, wherein NOx ppm are charted as a function of time. As illustrated in Figure 3, the catalyst system of this invention completely eliminated the ammonia spikes created during the rich pulses of the lean NOx adsorber. In this system, ammonia is stored on the NH_3 -SCR catalyst where it reacts with NOx during the 85 second lean duration, which thus improves the net NOx conversion from 55% to 80% with no additional fuel economy penalty. As shown in Figure 3, the improved net NOx conversion can be observed by the much narrower profile – zero ppm NOx is emitted for a significant amount of time as compared to the graph shown in Figure 1 of a system lacking the NH_3 -SCR + lean NOx adsorber combination.

[0038] The reaction between the stored ammonia and NOx increases the overall net NOx conversion, which is enhanced from 55% – the amount of NOx converted in prior art lean NOx trap systems – to 80% – as a result of the combination of a lean NOx trap and NH₃ –SCR catalyst system. Moreover, in addition to improving net NOx conversion, the ammonia stored in the NH₃ –SCR catalyst is depleted during the SCR reaction wherein ammonia and nitrogen oxide are reacted to produce nitrogen. The NH₃ –SCR catalyst is replenished with ammonia by subsequent rich pulses over the lean NOx adsorber that causes a portion of the NOx to react with hydrogen to form ammonia.

[0039] It should be noted that no urea or ammonia needs to be injected into the exhaust system to effectuate the reaction between ammonia and NOx. Rather, the ammonia is naturally generated from the NOx present in the exhaust gas as it passes over the lean NOx trap during rich pulses. More specifically, ammonia is naturally created during the fuel rich cycle of the lean NOx trap. Ammonia is naturally produced as it passes over the precious metal active component of the lean NOx trap. Similarly, the ammonia could also be generated in a conventional precious metal based TWC located upstream of a LNT/NH₃ –SCR system.

[0040] For this invention, the lean NOx trap is optimized for ammonia generation by removing oxygen storage capacity (OSC) and thereby enhancing the rich cycle, and thus creating a greater quantity of ammonia for reaction with the NOx in the downstream NH₃ –SCR catalyst. In a preferred embodiment, the lean NOx trap includes platinum as the precious metal. Platinum is the preferred precious metal because it is believed that a greater quantity of NH₃ is produced over platinum than rhodium, palladium and/or a combination of the precious metals. Nonetheless, other precious metals such as palladium and rhodium, and the combination of one or more of the precious metals platinum, palladium and rhodium may also be used to generate NH₃.

[0041] Additionally, the lean NOx trap of this invention preferably includes a "NOx adsorbing material" or NOx storage component/material, which can be alkali and alkali earth metals such as barium, cesium, and/or rare earth metals such as cerium and/or a composite of cerium and zirconium. Although an alternative catalyst

formulation that does not contain a NOx storage component but generates ammonia from NOx may also be utilized, in the most preferred embodiment, the NOx storage material should have the ability to store NOx at low temperature ranges, specifically in the range of 150 ° C–300 ° C. The NH₃ thermodynamic equilibrium under rich conditions is maximized during the temperature range of 150 ° C–300 ° C.

[0042] In general, to increase the NOx storage function of the lean NOx trap and effectuate the NOx conversion reaction, in the preferred embodiment, the lean NOx trap has the following characteristics: (1) the inclusion of platinum as the precious metal; (2) the ability to store NOx between 150 ° C and 500 ° C during the lean portion of the cycle; (3) the ability to maximize the duration of the lean NOx trap rich cycle; (4) the ability to generate ammonia at the 150 ° C–500 ° C temperature range; (5) minimize OSC to lessen fuel penalty; and (6) lower lambda to generate more ammonia. Ammonia production is maximized at the preferred temperature range, 150 ° C–300 ° C – which also correlates with the steady state equilibrium range for ammonia creation. It bears emphasis that other NOx storage components may be utilized, especially for stationary sources, where sulfur poisoning does not pose a threat.

[0043] Most simply, the NH₃-SCR catalyst may consist of any material or combination of materials that can adsorb ammonia and facilitate the NOx + NH₃ to yield nitrogen. The NH₃-SCR catalyst should preferably be made of a base metal catalyst on a high surface area support such as alumina, silica, titania, zeolite or a combination of these. More preferably, the NH₃-SCR catalyst should be made of a base metal selected from the group consisting of Cu, Fe and Ce and/or a combination of these metals, although other base metals may be used. Base metals generally are able to effectuate NOx conversion using ammonia while both the base metals and the high surface support material serves to store NH₃. The base metal and high surface area support such as zeolite selected should preferably be one that can store NH₃ over the widest possible temperature range. Likewise, the base metal selected is preferably one that can convert NO and NO₂ to N₂ across the widest possible temperature range and the widest range of NO/NO₂ ratios.

[0044] The advantage of the catalyst system of this invention is the use of a combination

[0047] Under the zoned catalyst designs shown in Figures 4a-4c, where alternating lean NOx and NH₃-SCR catalyst zones are provided, the ammonia formed by the lean NOx trap is believed to be immediately adsorbed by the NH₃-SCR catalyst for use in the NOx conversion reaction. It is further believed that the greater the separation between the lean NOx trap and the NH₃-SCR catalyst, the greater chance there is for the ammonia to be converted back into NOx. It is further believed that oxygen is more abundant in the back of a catalyst substrate and thus the oxygen may be available to effectuate the unwanted conversion of the ammonia back to nitrogen oxide. Accordingly, if the catalyst substrate is too long, there may be some undesired conversion that takes place; and thus in a preferred embodiment, the substrate is designed so that ammonia is available for immediate reaction with NOx.

[0048] Figures 5a-5c illustrate laboratory reactor data of the three different zoned catalyst system embodiments shown in Figures 4a-4c. This laboratory data was obtained with the three catalyst systems operating at a 250 ° C inlet gas temperature and operating with 50 second lean and 5 second rich cycles. Additionally, the inlet concentration of the NOx feed gas was 500 ppm and the overall space velocity was 15,000 per hour. As illustrated in Figures 5a-5c, with the use of a two-zoned catalyst system as depicted in Figure 5a, approximately 50 ppm of NO is emitted. This two-zone catalyst system resulted in a gross NOx conversion of 95% and a net NOx conversion of 66%. The four-zone catalyst embodiment, depicted as Figure 5b, significantly reduced NOx emissions, well below the 15 ppm range, to result in gross NOx conversion of 99% and a net NOx conversion of 86%. Finally, as illustrated by the eight zoned catalyst embodiment, Figure 5c, gross NOx conversion is 100% and net NOx conversion is 97.5%. The improvement comes from the reduction of N₂O, elimination of the NH₃ breakthrough and reduction of NOx. Accordingly, as the catalyst system is zoned down from 1" sections to ¼" sections, the test results revealed an associated improvement in net NOx conversion.

[0049] As shown in Figures 5a-5c, a zoned catalyst, with alternating lean NOx and NH₃-SCR catalysts in 1" to ¼" sections significantly improves the net NOx conversion from 66% to 97.5%. In addition, the gross NOx conversion is improved from 95% to 100%. In general, the improvement in the net NOx conversion is the function of the elimination of the ammonia slip, reduction in N₂O, and extra NOx reduction related to the NH₃

+ NOx reaction on the NH_3 -SCR catalyst. It is further believed that the drop in N_2O emissions is likely due to a higher fraction of the NOx reduction reaction proceeding on the NH_3 -SCR catalyst rather than the lean NOx trap. NOx reduction over a platinum-containing-lean NOx trap results in high levels of N_2O generation, whereas the NH_3 -SCR catalyst has a high selectivity to nitrogen.

[0050] Figures 6a-6c depicts laboratory data obtained using the three-zoned catalyst embodiments originally shown in Figures 4a-4c at a 200 ° C inlet gas temperature operating with a 25 second lean cycle and a 5 second rich cycle. As compared to Figures 5a-5c, it should be noted that shortening the lean time from 50 seconds, as used in Figures 5a-5c, to 25 seconds, resulted in a substantial higher steady emission of ammonia – a fact which results in reduced net NOx conversion rates, as compared to the data charted in Figures 5a-5c. As can be seen in Figures 6a-6c, the use of smaller zoned sections from two zones to eight zones, and thus 1" sections down to ¼ " sections, as illustrated in Figures 6a and 6c, improves the net NOx conversion from 50% to 81%. Again, this improvement is believed to come mainly from the reduction of ammonia breakthrough and a small reduction in N_2O emissions. This lab data was obtained with an inlet concentration of the NOx feed gas at 500 ppm and an overall space velocity at 15,000 per hour.

[0051] As set forth above, in the preferred embodiment, the lean NOx trap washcoat and NH_3 -SCR washcoat are combined in a single substrate rather than placing the NH_3 -SCR formulation downstream of the lean NOx adsorber as two separate catalyst substrates. Under this embodiment, the catalyst formulations can be incorporated together by mixing or layering the washcoats on a substrate.

[0052] Figures 7a-7c show three proposed washcoat configurations incorporating the lean NOx trap and NH_3 -SCR formulations into the same substrate. As shown in Figures 7a and 7b, the first and second proposed configurations have the lean NOx trap and NH_3 -SCR washcoat formulations on the bottom and top layer, respectively. It is believed that the top layer could be a highly porous structure that allows better and faster contact between the chemicals and gas phase and the active sites in the second layer. The third configuration, as shown in Figure 7c, involves the use of a one layer washcoat containing both lean NOx trap and NH_3 -SCR washcoat formulations.

Under this third configuration, shown in Figure 7c, the washcoat composition of the lean NOx trap and NH_3 -SCR catalyst could be homogeneously or heterogeneously mixed. For a heterogeneously mixed composition, the formulation of the lean NOx trap and NH_3 -SCR catalyst are separated. However, they contact each other in varying degrees by controlling the size of the grain structures. The homogeneously mixed composition allows for a more intimate contact between the two formulations and is thus preferred.

[0053] The invention also contemplates engineering such combinations within the pores of the monolithic substrate. An example of this is incorporating washcoat into porous substrates used for filtering diesel particulate matter. Thus, this lean NOx trap/ NH_3 -SCR catalyst concept can be integrated into diesel particulate matter devices.

[0054] This very active SCR reaction of NOx and ammonia proceeds with or without oxygen present. Koebel et al. reports that the fastest SCR reaction involves equal molar amounts of NO and NO_2 . NO and NO_2 then react with two NH_3 to yield N_2 in the absence of oxygen. In contrast, the lean NOx adsorber reaction of NOx plus CO is highly reactive only in an oxygen-free environment. In a lean NOx adsorber system, NOx is adsorbed during the lean cycle duration, NOx is not reduced. Accordingly, NOx reduction is limited to only the rich pulse time duration. On the other hand, the lean NOx adsorber + NH_3 -SCR catalyst system allows for NOx reduction reaction to proceed during both the lean and rich time durations. Accordingly, ammonia as a reductant can be considered as a much more robust reductant than carbon monoxide.

[0055] As set forth above, the fastest SCR reaction involves equal molar amounts of NO and NO_2 . Accordingly, Figure 8 illustrates the impact of varying NO: NO_2 ratios after hydrothermal aging. Figure 8 is a graph of three NH_3 -SCR catalyst formulations over a wide NO: NO_2 range. In the laboratory, it was possible to control the NO: NO_2 ratio entering the downstream NH_3 -SCR catalyst. Accordingly, the NO: NO_2 ratio entering the NH_3 -SCR catalyst was solely dependent on the upstream lean NOx adsorber. In some cases, the majority of the feed NOx (especially NOx spikes) are made up of mostly NO rather than NO_2 . Accordingly, it is believed that the catalyst formulations of this invention will enhance reported net NOx efficiency – and thus the preferred catalyst is one that is capable of operating across the broadest range of NO: NO_2

ratios, and at a full spectrum of temperature ranges.

[0056] In general, since NH_3 -SCR catalysts do not contain precious metals, they are significantly less costly than a typical lean NOx trap. Accordingly, it is more cost effective to have an overall catalyst system containing a lean NOx trap adsorber and an NH_3 -SCR catalyst system, rather than one that uses two lean NOx trap adsorbers. Additionally, the incorporation of both a lean NOx trap and NH_3 -SCR washcoat into a single substrate will significantly reduce substrate costs.

[0057] In another embodiment of this invention, NH_3 and NOx in an exhaust stream are reduced using a stoichiometric three-way catalyst system. This three-way catalyst system has particular application for high speed/high flow rate conditions (i.e., US06 conditions). Currently, three three-way catalysts are used for such high speed condition applications, wherein the third three-way catalyst is primarily directed to NOx removal for high speed/high flow rate conditions. Under this alternate embodiment, the third three-way catalyst can be substituted with an NH_3 -SCR catalyst to store NH_3 for reaction with NOx to improve net NOx conversion, eliminate NH_3 emissions and reduce catalyst costs.

[0058] To improve net NOx and NH_3 reduction, the second three-way catalyst can be modified to enhance the three-way catalyst's ability to generate NH_3 emissions. To this end, in a preferred embodiment, the three-way catalyst is designed to generate desirable NH_3 creation by using platinum as the precious metal of the three-way catalyst, by placing platinum on the outer layer of the three-way catalyst to maximize the $\text{NO} + \text{H}_2 \rightarrow \text{NH}_3$ reaction. Likewise, the oxygen storage capacity (OSC) of the three-way catalyst can be removed to further promote the creation of "desirable" NH_3 . By doing so, the NH_3 purposely generated during rich operation can then be stored by the NH_3 -SCR catalyst for subsequent reaction with NOx emissions, and thereby control both NOx and NH_3 emissions under all operating conditions.

[0059] When a car is operated under rich conditions, the air/fuel ratio is less than 14.6, hydrogen is produced in the exhaust via the water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The hydrogen that is produced then reacts with NOx as it passes over the precious metal surface to create "desirable" ammonia. The ammonia produced is then stored on an NH_3 -SCR catalyst to help reduce net NOx conversion. The reaction

of $\text{NO}_x + \text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ can then take place on a separate NH_3 selective catalyst, capable of converting NO_2 and NO to N_2 .

[0060] As shown in Figure 9, a stoichiometric three-way catalyst/ NH_3 -SCR catalyst system 10 is depicted, including a first three-way catalyst 14 positioned in close proximity to the engine 12 to reduce cold start emissions. The second three-way catalyst 16 is modified as described above to enhance the ability of the second three-way catalyst 16 to generate NH_3 emissions. Downstream of the second three-way catalyst 16 is an NH_3 -SCR catalyst 18 that functions to store NH_3 produced by the modified second three-way catalyst 16 for reaction with NO_x emissions, to reduce both NO_x and NH_3 emissions.

[0061] By substituting the third three-way catalyst as currently used with an NH_3 -SCR catalyst and thereby eliminating the need for a third precious metal containing catalyst, significant cost savings can be achieved.

[0062] It should further be noted that this invention also contemplates the use of a three-way catalyst, in combination with a lean NO_x trap and an NH_3 -SCR catalyst.

[0063] While the best mode for carrying out the invention has been described in detail, those familiar with the art to which this invention relates will recognize various alternative designs and embodiments for practicing the invention as defined by the following claims.